

for the five examples with the common structure* (Jones, Kearns & Wing, 1973; Enwall & van der Helm, 1974; the title molecule; Neuenschwander, Neuenschwander, Steinegger & Engel, 1979; Beagley *et al.*, 1982). In the cyclohexane ring of the average structure, the absolute torsion angles nearer to the bridge bond tend to be a little less than, and those remote from the bridge bond a little greater than, the $|\pm 55^\circ|$ calculated by molecular mechanics for cyclohexane itself (Beagley, 1978); the calculated torsion angles for free cyclohexene (0, 15, -45 , 60, -45 , 15°) are also similar to those in the fused structure (5, 10, -41 , 61, -47 , 14°). Thus, neither of the six-membered rings of this common structure is much strained by fusion. Of the three molecules with ring conformations* which differ from that of the common structure, capsidiol (Birnbaum, Stoessl, Grover & Stothers, 1974) still has a chair-half-chair conformation, but one of its rings is folded in the opposite sense to that in Fig. 3, perhaps under the influence of an isopropenyl side chain. The fluorinated structure of Hamor & Hamor (1976) has a much flatter cyclohexane ring, perhaps because of the possible conjugation involving its =O substituent. The structure of House, Phillips & Van Derveer (1979) has a twist-boat cyclohexane ring with a *tert*-butyl side chain.

Fig. 3(c) is a composite Newman projection of the title molecule which shows the rather exposed position of the bridgehead methyl group, projecting away from the folds of the two rings, on the rather convex side of the ring system. All five molecules with the common structure have a sterically similar bridgehead methyl group.

* Details of the individual molecules and their ring torsion angles are included with the deposited material (see deposition footnote).

Acta Cryst. (1982). B38, 1395–1397

Hexamethylenefurazan *N*-Oxide

BY MARJORIE M. HARDING*

IPI Chemistry Department, University of Liverpool, PO Box 147, Liverpool L69 3BX, England

AND R. MICHAEL PATON

Chemistry Department, Edinburgh University, West Mains Road, Edinburgh EH9 3JJ, Scotland

(Received 29 September 1981; accepted 8 December 1981)

Abstract. C₈H₁₂N₂O₂, monoclinic, $P2_1/n$, $a = 11.50(2)$, $b = 10.50(2)$, $c = 7.07(1)$ Å, $\beta = 101.0(3)^\circ$, $Z = 4$, $D_c = 1.33$ g cm⁻³. Final $R = 0.056$

We thank the SERC for support.

References

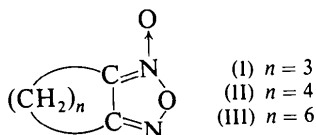
- BEAGLEY, B. (1978). *Mol. Struct. Diffr. Methods*, **6**, 63–92.
 BEAGLEY, B., PRITCHARD, R. G., RAMAGE, R. & SOUTHWELL, I. A. (1982). *Acta Cryst.* B38, 1391–1393.
 BIRNBAUM, G. I., STOESSL, A., GROVER, S. H. & STOTHERS, J. B. (1974). *Can. J. Chem.* **52**, 993–1005.
 Crystal Structure Search Retrieval (1980). *CSSR Instruction Manual*. Daresbury Laboratory, England.
 ENWALL, E. L. & VAN DER HELM, D. (1974). *Recl. Trav. Chim. Pays-Bas*, **93**, 53–56.
 HAMOR, M. J. & HAMOR, T. A. (1976). *Acta Cryst.* B32, 2886–2889.
 HOUSE, H. O., PHILLIPS, W. V. & VAN DERVEER, D. G. (1979). *J. Org. Chem.* **44**, 2400–2405.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
 JONES, C. R., KEARNS, D. R. & WING, R. M. (1973). *J. Chem. Phys.* **58**, 1370–1383.
 KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521–523.
 MACSWEENEY, D. F., RAMAGE, R. & SATTAR, A. (1970). *Tetrahedron Lett.* pp. 557–560.
 MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1978). *MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
 MORTON, P. (1980). Private communication.
 NEUENSCHWANDER, M., NEUENSCHWANDER, A., STEINEGGER, E. & ENGEL, P. (1979). *Helv. Chim. Acta*, **62**, 609–626.
 OLDENZIEL, O. H., VAN LEUSEN, D. & VAN LEUSEN, A. M. (1977). *J. Org. Chem.* **42**, 3114–3118.
 SHEDRICK, G. M. (1976). *SHELX*. A program for crystal structure determination. Univ. of Cambridge, England.
 SOUTHWELL, I. A. (1978). *Aust. J. Chem.* **31**, 2527–2538.

* To whom correspondence should be addressed.

for 523 observed reflections. The furazan *N*-oxide ring geometry is compared with that of the tetra- and trimethylene analogues whose structures have recently been determined [Barrow (1982). *Acta Cryst.* B38, 308–310; Barnes, Barrow, Harding, Paton, Ashcroft,

Crosby & Joyce (1979). *J. Chem. Res. (S)*, pp. 314–315]. Increasing thermal instability (hexa- to tri-compound), involving fission of the N(2)–O(1) bond, can be correlated with increasing length of this bond, 1.428 (7), 1.465 (4) and 1.494 (3) Å, which in turn results from different geometrical constraints in the eight-, six-, and five-membered rings.

Introduction. We are making a comparative study of bond lengths and stereochemistry in relation to chemical structure and thermal stability in furazans and furazan *N*-oxides (furoxans). The structures of (I) (at 150 K) and (II) (at 125 K) have been reported (Barnes *et al.*, 1979; Barrow, 1982). The room-temperature study of (III) is reported here.



The material was prepared from 1,2-cyclooctanedione dioxime by treatment with cold aqueous sodium hypochlorite (Boyer & Toggweiler, 1957), and recrystallized from hexene (m.p. 307 K).

Weissenberg photographs of the layers $hk0$ to $hk5$ were taken with Cu $K\alpha$ radiation, and a crystal of approximate dimensions $0.04 \times 0.04 \times 0.22$ mm mounted in a glass capillary; they were measured by the SRC Microdensitometer Service to give 526 unique reflections. Lp corrections were applied; no absorption correction was made. The multisolution direct-methods procedure in *SHELX* (Sheldrick, 1976) gave an *E* map in which all C, N and O atoms could be recognized. Least-squares refinement of these atom positions, individual isotropic thermal parameters and layer scale factors reduced *R* from 0.32 to 0.10, and a difference Fourier series showed peaks at or near the expected

Table 1. *Atom positions* ($\times 10^4$) *and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = 8\pi^2 \bar{U}$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} (Å ²)
O(1)	−1380 (4)	−45 (4)	1713 (7)	5.8 (2)
O(2)	387 (5)	−1032 (3)	2118 (7)	6.8 (2)
N(2)	−125 (5)	−55 (3)	2369 (8)	4.5 (2)
N(5)	−1797 (5)	1129 (5)	2176 (8)	5.4 (3)
C(3)	170 (5)	1055 (4)	3143 (8)	3.8 (2)
C(4)	−860 (4)	1766 (4)	3012 (8)	3.9 (2)
C(6)	−967 (6)	3086 (5)	3717 (10)	4.7 (3)
C(7)	−523 (5)	4106 (5)	2511 (9)	4.6 (3)
C(8)	782 (6)	4152 (4)	2533 (10)	4.6 (3)
C(9)	1267 (5)	3131 (4)	1344 (9)	4.4 (3)
C(10)	1992 (5)	2098 (5)	2474 (10)	4.7 (3)
C(11)	1404 (5)	1411 (4)	3928 (9)	3.9 (3)

Table 2. *Geometry of the hexamethylenefurazan N-oxide molecule*

(a) Bond lengths (Å)			
O(1)–N(2)	1.428 (7)	C(6)–C(7)	1.517 (8)
N(2)–C(3)	1.304 (6)	C(7)–C(8)	1.498 (8)
C(3)–C(4)	1.389 (7)	C(8)–C(9)	1.531 (5)
C(4)–N(5)	1.309 (6)	C(9)–C(10)	1.502 (7)
N(5)–O(1)	1.385 (7)	C(10)–C(11)	1.517 (9)
N(2)–O(2)	1.213 (6)	C(11)–C(3)	1.470 (7)
C(4)–C(6)	1.485 (7)		
C–H mean 1.00 Å, range 0.96–1.02 Å			
(b) Bond angles (°)			
O(1)–N(2)–C(3)	107.2 (4)	C(4)–C(6)–C(7)	114.3 (6)
O(1)–N(2)–O(2)	116.6 (4)	C(6)–C(7)–C(8)	117.5 (5)
O(2)–N(2)–C(3)	136.2 (6)	C(7)–C(8)–C(9)	116.2 (5)
N(2)–C(3)–C(4)	107.6 (4)	C(8)–C(9)–C(10)	115.9 (5)
C(3)–C(4)–N(5)	111.9 (4)	C(9)–C(10)–C(11)	115.4 (5)
C(4)–N(5)–O(1)	105.7 (5)	C(10)–C(11)–C(3)	112.9 (5)
N(5)–O(1)–N(2)	107.7 (3)	C(11)–C(3)–C(4)	129.6 (4)
C(3)–C(4)–C(6)	127.1 (4)		
C–C–H mean 109°, range 103–115°			
H–C–H mean 108°, range 100–120°			
(c) Torsion angles (°) (e.s.d.'s < 1°)			
C(3)–C(4)–C(6)–C(7)	74	C(8)–C(9)–C(10)–C(11)	53
C(4)–C(6)–C(7)–C(8)	−68	C(9)–C(10)–C(11)–C(3)	46
C(6)–C(7)–C(8)–C(9)	76	C(10)–C(11)–C(3)–C(4)	−85
C(7)–C(8)–C(9)–C(10)	−108	C(11)–C(3)–C(4)–C(6)	−2

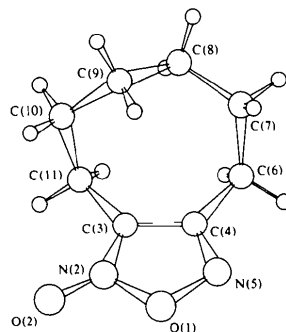


Fig. 1. The hexamethylenefurazan *N*-oxide (III) molecule.

hydrogen positions and no others. H atoms were introduced and their coordinates refined with the restraint $d_{C-H} = 1.00$ (3) Å; at the same time positions and anisotropic vibration parameters of the other atoms were refined, and the overall scale factor. The weighting $W = 1/0.04F^2$ was used for each reflection. The final *R* factor is 0.056 for 523 reflections.

Atom parameters are given in Table 1, and some details of the molecular geometry in Table 2.*

* Lists of structure factors, anisotropic thermal parameters and H-atom positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36574 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Comparison of geometry in three furoxans

Compound	N(2)—O(1)	C(3)— C(4)—C(6)	C(<i>n</i>)— C(3)—C(4)
(I)	1.494 (3) Å	110.7 (2)°	113.3 (2)°
(II)	1.465 (4)	122.2 (2)	126.1 (2)
(III)	1.428 (7)	127.1 (4)	129.6 (4)

The molecule is illustrated in Fig. 1, drawn by *PLUTO* (Motherwell, 1976).

Discussion. Thermal instability, involving initially the fission of the bond N(2)—O(1), increases in the furoxans from (III) to (I). This can be directly correlated with the lengthening of the bond N(2)—O(1) as shown in Table 3; it appears to be brought about by the different constraints on the angles at C(3) and C(4) imposed by the eight-, six- and five-membered rings respectively. In all other respects the three furazan rings have the same geometry within experimental error; in all three the angle C(3)—N(2)—O(2) is very large, (I) 138.0 (3)°, (II) 134.8 (3), (III) 136.2 (6)°.

The atoms O(1), N(2), C(3), C(4) and N(5) of the furoxan ring of (III) are coplanar (within 0.005 Å) but O(2) is 0.028 Å from their plane.

In an eight-membered ring the C—C—C—C torsion angles cannot all take the optimum values of ± 60 and 180° , with C—C=C—C at 0° ; Table 2(c) shows the substantial variations from these values.

References

- BARNES, J. F., BARROW, M. J., HARDING, M. M., PATON, R. M., ASHCROFT, P. L., CROSBY, J. & JOYCE, C. J. (1979). *J. Chem. Res. (S)*, pp. 314–315; (*M*), pp. 3601–3621.
- BARROW, M. J. (1982). *Acta Cryst.* B38, 308–310.
- BOYER, J. H. & TOGGWEILER, U. (1957). *J. Am. Chem. Soc.* 79, 895–897.
- MOTHERWELL, W. D. S. (1976). *PLUTO. Program for Plotting Molecular and Crystal Structures*. Univ. of Cambridge, England.
- SHELDRICK, G. M. (1976). *SHELX. A program for crystal structure determination*. Univ. of Cambridge, England.